A Novel Synthesis of Tetraaminoethenes by Reduction of Oxalic Amidines and Subsequent Electrophilic Substitution☆

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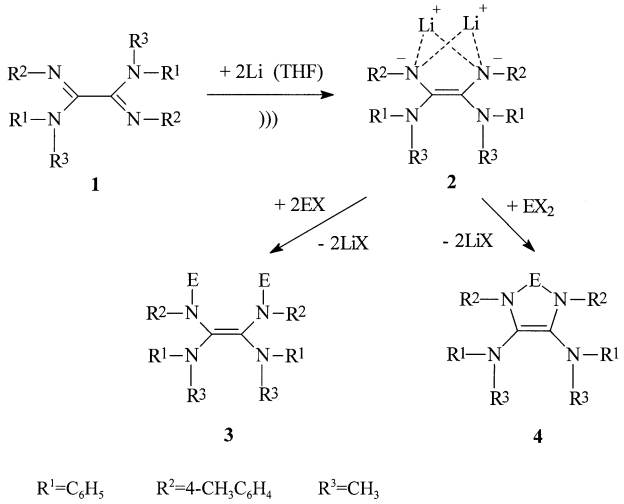
Reduction of the 1,4-diaza-1,3-butadiene substructure of hexasubstituted amidines **1** with lithium metal yields the dilithium diamides **2**. Subsequent reactions of these with various electrophiles give the title substances **3**, **4** and **5**. The quenching reaction of **2** with organosilicon derivatives leads to open-chain **3b** as well as to cyclic tetraaminoethenes **4a**,**b**. Treatment of **2** with methanol gives **3a** which in the presence of oxygen is reoxidized to the starting amidine **1**. Using alkyl halides as electrophiles, compounds **3c−e** and **4c**,**d** could be obtained in moderate to good yields. X-ray structural analyses of derivatives **3e** and **4c** reveal sterically overloaded central C−C double bonds. Whereas phosgene and its thio derivative give the imidazolines **4e**,**f**, methyl benzoate allows a stepwise substitution leading to tetraaminoethenes bearing different residues at the nitrogen atoms.

Tetraaminoethenes are characterized by a wide range of applications in synthetic, organometallic and physical organic chemistry[1]. Therefore, an extensive chemistry of these electron-rich derivatives has been developed. Thus, they are powerful nucleophiles and π bases, as well as strong reducing agents. In addition, some derivatives serve as chemiluminescent species in light-emitting systems.

The first tetraaminoethenes were synthezised in 1950 by Pruett[2a] by the aminolysis of chlorotrifluoroethene with dimethylamine, but this method is limited to just a few secondary amines. Two general preparative routes for the synthesis of tetraaminoethenes are based on the dimerization of in situ generated carbenoids[2b][2c]. Starting from derivatives of either orthoformic acid and various diamines, or strong bases and a formamidinium cation, an imidazolium/pyrimidinium salt, a considerable number of acyclic[1c], monocyclic[3], polycyclic[4][5] and optically active[6] tetraaminoethenes could be isolated. In this paper, we describe a new synthetic access to the title compounds via a reduction/substitution sequence starting from oxalic amidines **1**. Due to their acceptor properties, 1,4-diaza-1,3-dienes such as the bis(imines) of glyoxal, diacetyl and benzil may be readily reduced by alkali metals[7]. Hexasubstituted oxalic amidines of type **1**, containing the same structural motif, yield the crystalline and stable dianion **2** following treatment with metallic lithium under ultrasonic conditions[3]. As shown in Scheme 1, the substructure of tetraaminoethenes already exists in the diamide **2**. Therefore, this dinucleophilic building block offers many possibilities for preparing structurally new tetraaminoethenes.

Scheme 1



1 **2** **3** **4**

3	E	X
a	H	CH_3O
b	$(CH_3)_3Si$	Cl
c	CH_3	I
d	C_2H_5	I
e	C_3H_7	I
f	C_6H_5CO	Cl

4	E	X
a	$(CH_3)_2Si$	Cl
b	$(CH_3)_2Si(CH_2)_2$-$Si(CH_3)_2$	Cl
c	$(CH_2)_3$	Br
d	$(CH_2)_4$	Br
e	C=O	Cl
f	C=S	Cl

Using THF as the solvent and metallic lithium as the reducing agent, the persubstituted oxalic amidine **1** was converted straightforwardly via the EPR-spectroscopically detectable dark-colored radical anion to the red dianion **2**.

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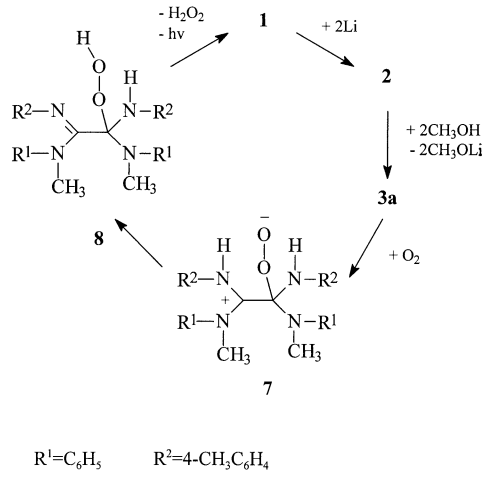
Treatment of **2** with methanol as a proton source gave a yellowish solution, which exhibited a strong greenish fluorescence. Attempts to isolate the compound **3a** by recrystallization or by chromatographic methods were not successful and led only to the starting material **1**. However, work-up under anaerobic conditions (argon as inert gas) yielded **3a**. In the presence of oxygen, **3a** was immediately oxidized with visible chemiluminescence. A similiar behavior was described by Smith and MacPherson[8] for the oxidation reaction of α,α′-dianilinostilbene. In this case, despite the starting material formed by hydrolysis being the major product, a stable hydroperoxide was isolated besides α,α′-dianilinostilbene. In contrast, the oxidation of **3a** regenerated **1** as the sole product. The suggested mechanistic pathway is given in Scheme 2. In the first step, oxygen adds to **3a**, leading to the dipolar intermediate **7**. The formation of a 1,2-dioxetane can be excluded because in no case did the characteristic C−C bond cleavage take place. A subsequent H-shift led first to **8** and ultimately to hydrogen peroxide and the starting amidine **1**. The driving force of this at first sight surprising oxidation reaction may be the unusual stability of the amidine/amidinium substructure.

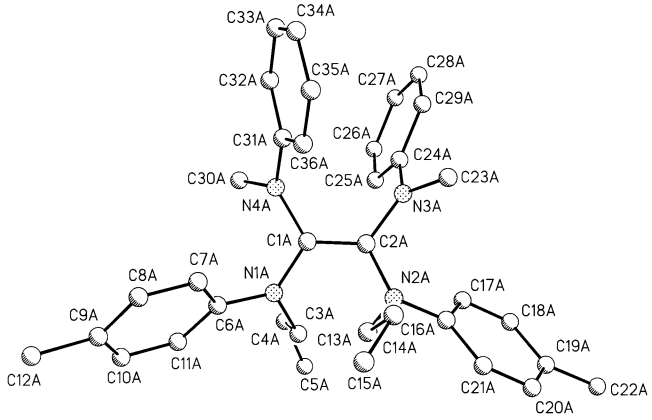
Scheme 2



For the quenching reaction of the dianion **2**, organosilicon derivatives proved to be especially favorable. For example, the reactions with chlorotrimethylsilane or 1,2-bis(chlorodimethylsilyl)ethane proceeded in nearly quantitative yields, furnishing the stable and highly fluorescent compounds **3b** and **4b**. The conversion of **2** using dichlorodimethylsilane led to the air-sensitive five-membered ring system **4a**.

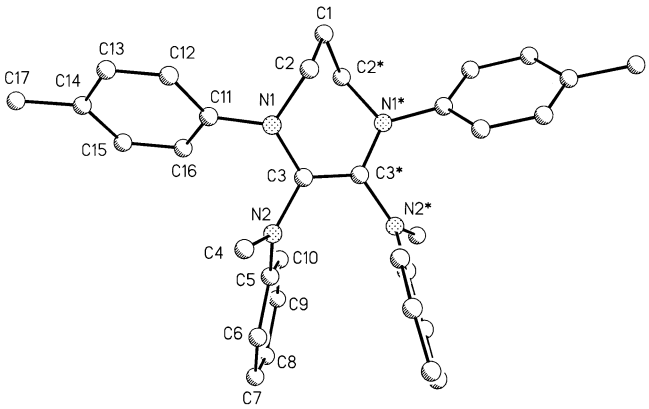
As described recently[3], the alkylation of **2** constitutes a convenient and novel route to tetraaminoethenes. Thus, as representative compounds the derivatives **3c−e** and **4c**,**d** were synthesized by simple alkylation of **2** with alkyl halides. Amidines often show two or more distinct ^{1}H- and ^{13}C-NMR resonances for all of the non-equivalent nuclei of several isomeric forms[9][10]. The starting material **1**, as well as the products **3−6**, have such substructures, and therefore show different resonances in their spectra. Many of the ^{1}H- and ^{13}C-NMR spectra are, therefore, very complex, even though the purity of the products was verified by TLC and combustion analyses. We were unable to detect mixtures of *E*/*Z* diastereomers (**3c−e**), neither by TLC nor by HPLC. Compounds **3e** and **4c** were further investigated as illustrative examples, using X-ray structural analysis. Figure 1 shows the X-ray crystal structures of **3e** and of the seven-membered ring system **4c**, obtained by reaction of **2** with 1,3-dibromopropane. Both compounds are characterized by a sterically overloaded C=C double bond, leading to a restricted rotation of the C−N single bonds. Moreover, this steric shielding explains the stability of **3** towards oxygen and other electrophiles. The structure of **3e** clearly shows that the *Z* arrangement in the product reflects the configuration into the starting dianion **2**. All these data imply that the alkylation of **2** proceeds stereospecifically.

Figure 1. Molecular structure of **3e**[a]



[a] Selected distances [Å] and angles [°]: C(1A)−C(2A) 1.344(4), C(1A)−N(1A) 1.408(4), C(1A)−N(4A) 1.416(4), C(2A)−N(2A) 1.414(4), C(2A)−N(3A) 1.401(4); C(2A)−C(1A)−N(1A) 122.7(3), C(1A)−C(2A)−N(2A) 121.0(3), C(2A)−C(1A)−N(4A) 122.6(3), C(1A)−C(2A)−N(3A) 122.4(3), N(1A)−C(1A)−N(4A) 114.6(3), N(3A)−C(2A)−N(2A) 116.5(3), N(1A)−C(1A)−C(2A)−N(2A) 25.9(3).

Figure 2. Molecular structure of **4c**[a]



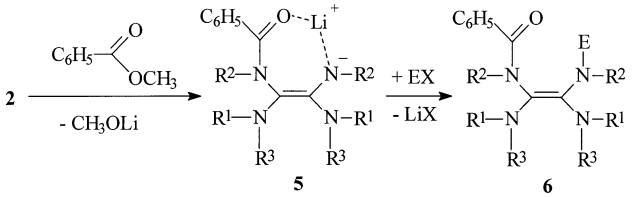
[a] Selected distances [Å] and angles [°]: C3−C3* 1.355(7), N1−C3 1.408(4), N2−C3 1.402(5), N1−C3 1.408(4), N1−C2 1.465(5), C1−C2 1.510(5); C3*−C3−N1 123.2(2), C3*−C3−N2 122.2(2), C3−C3*−N1 123.2(2), N1−C3−C3*−N1* 23.9(2).

In the case of 1,2-dibromoethane or 1,2-dibromocyclohexane, all attempts at alkylation were in vain. Probably, the tetrahydropyrazine intermediates underwent a cyclore-

version process leading to unsaturated compounds and the starting amidine **1**. For example, by using 1,2-dibromocyclohexane as an alkylating agent, besides **1**, cyclohexene was identified by gas chromatography.

Acylation of **2** with phosgene and thiophosgene gave the imidazolone **4e** and the -thione **4f** in good yields. The toxic and gaseous phosgene can be replaced by the less dangerous oxalyl chloride. It is noteworthy that the ^{13}C-NMR spectra of **4e**,**4f** revealed a strong shielding of the carbonylic (δ = 148.9) as well as of the thiocarbonylic (δ = 163.1) carbon atoms, respectively. In both heterocyclic systems, the formal separation of charges (**4e/4f**) is further favored by an aromatization, as recently demonstrated by Kuhn[11].

Scheme 3



R^1=C_6H_5 R^2=4-$CH_3C_6H_4$ R^3=CH_3

6	E	X
a	H	CH_3O
b	CH_3	I
c	$C_6H_5CH_2$	Br

Beyond this, we tested other electrophiles as quenching agents for the dianion **2**. The reaction with methyl benzoate yielded the monobenzoylated product **5**, which did not react with further methyl benzoate but reacted with methanol to give the unstable **6a**. A second acylation reaction leading to the bis(benzoyl) derivative **3f** was achieved using the more strongly electrophilic benzoyl chloride. On the other hand, the nucleophilicity of **5** allowed the introduction of a second substructure, as demonstrated by reactions with methyl iodide and benzyl bromide, which led to compounds **6b**,**c**.

We are indebted to the the *Fonds der Chemischen Industrie* for the financial support of this work.

Experimental Section

CHN Analyses: Leco CHN automatic analyser CHNS-932. − MS: Finnigan MAT SSQ 710. − IR spectra: Nicolet Impact 400. − Melting points (uncorrected): Cambridge Instruments micro hot stage Galen III according to Boetius. − Chemical yields are not optimized. − All reactions were monitored by TLC carried out on 0.25-mm Merck silica-gel plates (60 F_{254}) using UV light. − Column chromatography: 0.040−0.063-mm Merck silica gel. − Solvents were dried and freshly distilled prior to use. THF was distilled from Na/benzophenone. − ^{1}H and ^{13}C NMR: Bruker AC 250 and DRX 400; 5-mm multinuclear probe head. ^{1}H-NMR shifts: relative to ^{1}H signals of the solvent. − X-ray diffraction data for **3e** and **4c**: For the data collection a Nonius-CAD4 diffractometer was used (using graphite-monochromated Mo-K_α radiation). The crystals were mounted in a glass capillary (20°C). Data were corrected for Lorentz and polarization effects, but not for absorption[12]. The structures were solved by direct methods (SHELXS[13]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[14]). The hydrogen atoms of **3e** and of the methyl group C17 of **4c** were included at calculated positions with fixed thermal parameters. The other hydrogen atoms of **3e** were located from the difference Fourier map and were refined isotropically. All non-hydrogen atoms were refined anisotropically. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **4c**[15]: $C_{33}H_{36}N_4$, M_r = 488.66 g mol^{-1}, colorless prism, size 0.40 × 0.30 × 0.20 mm, monoclinic, space group *C2/c* (No. 15), a = 16.087(1), b = 13.796(2), c = 14.025(1) Å, β = 117.74(1)°, V = 2754.9 (5) Å^3, Z = 4, $\rho_{calcd.}$ = 1.178 g cm^{-3}, μ (Mo-K_α) = 0.70 cm^{-1}, F(000) = 1048, 2892 reflections in $-h$, $-k$, $\pm l$, measured in the range 2.86° ≤ Θ ≤ 26.28°, 2793 independent reflections, R_{int} = 0.052, 1189 reflections with $F_o > 4\ \sigma\ (F_o)$, 228 parameters, $R_{obs.}$ = 0.071, $wR^2_{obs.}$ = 0.176, *GooF* = 1.18, largest difference peak and hole: 0.27 eÅ^{-3}, −0.28 eÅ^{-3}.

Crystal Data for **3e**[15]: $C_{36}H_{44}N_4$, M_r = 532.75 g mol^{-1}, colorless prism, size 0.40 × 0.36 × 0.34 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 11.268(2), b = 14.328(1), c = 20.023(3) Å, α = 99.45(1), β = 91.32(1), γ = 96.16(1)°, V = 3167.7 (8) Å^3, Z = 4, $\rho_{calcd.}$ = 1.117 g cm^{-3}, μ (Mo-K_α) = 0.66 cm^{-1}, F(000) = 1152, 11328 reflections in $+h$, $-k$, $\pm l$, measured in the range 2.32° ≤ Θ ≤ 24.67°, 10726 independent reflections, R_{int} = 0.033, 4412 reflections with $F_o > 4\ \sigma\ (F_o)$, 721 parameters, $R_{obs.\ =\ 0}$.058, $wR^2_{obs.}$ = 0.124, *GooF* = 1.15, largest difference peak and hole: 0.44 eÅ^{-3}, −0.21 eÅ^{-3}.

Dilithium Complex (**2**)[3]: In a 250-ml Schlenk vessel, 0.5 g (1.1 mmol) of **1** was dissolved in ca. 30 ml of THF under argon and 0.3 g (4.3 mmol) of lithium was added. Reaction was initiated by means of an ultrasonic bath. After 3 h, a clear red solution was obtained, from which excess lithium was removed by filtration.

General Procedure for the Synthesis of Compounds **3**, **4** *and* **6**: To a solution of 1.1 mmol of **2**, 2.2 mmol of a monofunctional or 1.1 mmol of a bifunctional electrophile (compounds **3**, **4**) or 1.1 mmol of methyl benzoate (compounds **6b**,**c**) was added under stirring at −78°C. In the case of **6b**,**c**, the appropriate electrophile was added after 60 min. After completion of the addition, the mixture was allowed to warm to room temp. and stirring was continued until the solution was almost colorless. The solvent was then removed in vacuo, the residue was taken up in toluene, and the lithium salt was filtered off. The tetraaminoethenes were purified by column chromatography on silica gel (toluene as the mobile phase) or by recrystallization from *n*-heptane (**4a**).

N^1,N^2-Dimethyl-$N^{1\prime}$,$N^{2\prime}$-bis(4-methylphenyl)-N^1,N^2-diphenyl-1,1,2,2-ethenetetramine (**3a**): To a solution of 1.1 mmol of **2**, 2.2 mmol of methanol was added with stirring at −78°C. After completion of the addition, the reaction mixture was allowed to warm to room temp. The solvent was evaporated and the residue was extracted with *n*-heptane under inert conditions (argon stream). Yield 88% (0.44 g), highly air-sensitive yellow oil. − ^{1}H NMR ([D$_8$]THF, 250 MHz): δ = 2.23 (s, 6 H), 2.81 (s, 6 H), 6.41 (s, 2 H), 6.47−6.61 (m, 6 H), 6.72−6.78 (m, 8 H), 6.97−7.04 (m, 4 H). − ^{13}C NMR ([D$_8$]THF, 62 MHz): δ = 20.55, 36.80, 115.34, 118.11, 122.53, 123.53, 125.96, 128.88, 129. 67, 142.81, 147.88.

N^1,N^2-Dimethyl-$N^{1\prime}$,$N^{2\prime}$-bis(4-methylphenyl)-N^1,N^2-diphenyl-$N^{1\prime}$,$N^{2\prime}$-bis(1,1,1-trimethylsilyl)-1,1,2,2-ethenetetramine (**3b**): Yield 94% (0.62 g), colorless crystals, m.p. 181°C. − ^{1}H NMR ($CDCl_3$,

250 MHz): δ = −0.18 (s, 18 H), 2.35 (s, 6 H), 2.81 (s, 6 H), 6.75−7.26 (m, 18 H). − ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 1.97, 20.55, 33.80, 115.45, 117.02, 118.01, 121.77, 123.60, 127.46, 128.20, 129.28, 131.00. − MS (CI with H_2O); *m/z* (%): 594 (36) [M^+ + 1], 593 (100) [M^+], 592 (45), 577 (23), 486 (51), 470 (33), 414 (37), 281 (13), 235 (13), 223 (50), 208 (22), 93 (59). − $C_{36}H_{48}N_4Si_2$ (593.0): calcd. C 72.92, H 8.16, N 9.45; found C 73.31, H 8.49, N 9.28.

N¹,N1′,N²,N²′-Tetramethyl-N¹′,N²′-bis(4-methylphenyl)-N¹,N²-diphenyl-1,1,2,2-ethenetetramine (**3c**): Yield 90% (0.48 g), pale-yellow crystals, m.p. 83°C, further analytical data are in agreement with literature data.[3]

N¹′,N²′-Diethyl-N¹,N²-dimethyl-N¹′,N²′-bis(4-methylphenyl)-N¹,N²-diphenyl-1,1,2,2-ethenetetramine (**3d**): Yield 91% (0.51 g), colorless crystals, m.p. 218°C. − ^{1}H NMR ($CDCl_3$, 400 MHz, −40°C): δ = 0.31−0.38 (m, 3 H), 0.85−0.94 (m, 1 H), 1.24−1.26 (m, 2 H), 1.35−1.38 (m, 1 H), 2.12−2.29 (m, 6 H), 2.42 (s, 1 H), 2.56 (s, 1 H), 2.81−3.06 (m, 1 H), 3.17−3.37 (m, 4 H), 3.59−3.61 (m, 1 H), 3.85−3.87 (m, 1 H), 6.54−7.20 (m, 18 H). − ^{13}C NMR ($CDCl_3$, 100 MHz, −40°C): δ = 11.70, 11.86, 13.40, 13.77, 14.56, 20.61, 20.84, 22.99, 32.12, 32.45, 39.51, 40.01, 40.85, 47.61, 114.08, 114.42, 114.99, 115.44, 116.47, 116.86, 117.62, 117.79, 117.93, 118.16, 126.94, 127.73, 128.01, 128.66, 128.95, 129.71, 129.81, 141.09, 146.09. − MS (CI with CH_4); *m/z* (%): 506 (13) [M^+ + 2], 505 (56) [M^+ + 1], 504 (100) [M^+], 106 (16). − $C_{34}H_{40}N_4$ (504.7): calcd. C 80.91, H 7.99, N 11.10; found C 81.01, H 8.22, N 10.89.

N¹,N²-Dimethyl-N¹′,N²′-bis(4-methylphenyl)-N¹,N²-diphenyl-N¹′,N²′-di-n-propyl-1,1,2,2-ethenetetramine (**3e**): Yield 83% (0.49 g), yellow crystals, m.p. 151°C. − ^{1}H NMR ([D_8]THF, 250 MHz): δ = 0.49 (s, 2 H), 0.80 (s, 5 H), 1.16 (s, 1 H), 1.82 (m, 2 H), 2.17 (s, 6 H), 2.55 (s, 3 H), 2.92 (s, 2 H), 3.16 (s, 3 H), 3.47 (s, 1 H), 3.82 (s, 1 H), 6.52−7.16 (m, 18 H). − ^{13}C NMR ([D_8]THF, 62 MHz): δ = 11.67, 20.54, 22.09, 40.87, 49.14, 56.06, 115.56, 116.17, 117.36, 118.73, 127.88, 128.66, 129.28, 129.96, 143.97, 147.68. − MS (CI with H_2O); *m/z* (%): 534 (35) [M^+ + 2], 533 (94) [M^+ + 1], 532 (80) [M^+], 589 (50), 426 (72), 384 (92), 278 (10), 266 (31), 223 (100), 208 (16), 118 (22), 106 (28), 91 (17). − $C_{36}H_{44}N_4$ (532.8): calcd. C 81.16, H 8.32, N 10.51; found C 81.23, H 8.39, N 10.47.

N-{2-[Benzoyl(4-methylphenyl)amino]-1,2-bis[methyl(phenyl)-amino]ethenyl}-N-(4-methylphenyl)benzamide (**3f**): Yield 76% (0.55 g), yellow crystals, m.p. 254°C. − IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (s, 6 H), 2.95 (s, 6 H), 6.80−7.00 (m, 14 H), 7.15−7.54 (m, 14 H). − ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 20.92, 40.58, 114.89, 118.78, 125.30, 127.32, 128.23, 128.78, 129.04, 129.36, 129.68, 131.89, 135.53, 136.62, 137.86, 138.87, 145.20, 172.05. − MS (CI with H_2O); *m/z* (%): 658 (33) [M^+ + 2], 657 (100) [M^+ + 1], 656 (34) [M^+], 253 (53), 223 (15), 194 (92), 117 (84). − $C_{44}H_{40}N_4O_2$ (656.8): calcd. C 80.46, H 6.14, N 8.53; found C 80.61, H 6.02, N 8.60.

2,3-Dihydro-N⁴,N⁵,2,2-tetramethyl-1,3-bis(4-methylphenyl)-N⁴,N⁵-diphenyl-1H-1,3,2-diazasilole-4,5-diamine (**4a**): Yield 63% (0.35 g), air-sensitive colorless solid. − ^{1}H NMR ([D_8]THF, 250 MHz): δ = 0.45 (s, 6 H), 2.17 (s, 6 H), 2.70 (s, 6 H), 6.51−6.57 (m, 2 H), 6.69 (d, ^3J = 12.92 Hz, 4 H), 6.83−7.03 (m, 12 H). − ^{13}C NMR ([D_8]THF, 62 MHz): δ = 1.46, 20.70, 37.73, 113.76, 117.62, 124.71, 127.54, 128.95, 130.00, 132.27, 140.57, 148.85. − MS (CI with CH_4); *m/z* (%): 505 (12) [M^+ + 1], 504 (20) [M^+], 447 (34), 342 (78), 340 (15), 281 (7), 235 (18), 223 (45), 151 (12), 149 (17), 136 (31), 108 (100).

1,2,3,4,5,6-Hexahydro-N⁷,N⁸,2,2,5,5-hexamethyl-1,6-di(4-methylphenyl)-N⁷,N⁸-diphenyl-1,6,2,5-diazadisilocine-7,8-diamine (**4b**): Yield 89% (0.58 g), colorless crystals, m.p. 186°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.22 (s, 12 H), 1.29 (s, 4 H), 2.22 (s, 6 H), 2.67 (s, 6 H), 6.58 (d, ^3J = 7.8 Hz, 8 H), 6.71 (t, ^3J = 6.7 Hz, 2 H), 6.86 (d, ^3J = 8.1 Hz, 4 H), 7.02−7.06 (m, 4 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.17, 13.42, 20.66, 34.28, 117.42, 118.28, 126.02, 127.50, 128.59, 130.28, 131.98, 145.61, 148.22. − MS (CI with H_2O); *m/z* (%): 592 (42) [M^+ + 1], 591 (86) [M^+], 590 (42), 575 (32), 484 (100), 342 (5), 305 (7), 295 (21), 252 (9), 250 (32), 223 (21), 163 (6), 93 (27). − $C_{36}H_{46}N_4Si_2$ (591.0): calcd. C 73.17, H 7.85, N 9.48; found C 73.31, H 7.85, N 9.30.

4,5,6,7-Tetrahydro-N²,N³-dimethyl-1,4-bis(4-methylphenyl)-N²,N³-diphenyl-1H-1,4-diazepine-2,3-diamine (**4c**): Yield 65% (0.36 g), pale-yellow crystals, m.p. 215°C, further analytical data are in agreement with literature data.[3]

1,4,5,6,7,8-Hexahydro-N²,N³-dimethyl-1,4-bis(4-methylphenyl)-N²,N³-diphenyl-1,4-diazocine-2,3-diamine (**4d**): Yield 37% (0.21 g), pale-yellow crystals, m.p. 175°C. − ^{1}H NMR ([D_6]acetone, 400 MHz, −40°C): δ = 1.04 (m, 2 H), 1.80 (m, 2 H), 2.04 (s, 6 H), 2.87 (s, 6 H), 3.24 (t, ^3J = 13.1 Hz, 2 H), 4.30 (d, ^3J = 13.7 Hz, 2 H), 6.52−6.59 (m, 4 H), 6.71 (d, ^3J = 8.1 Hz, 2 H), 6.78−6.86 (m, 6 H), 7.02 (d, ^3J = 7.6 Hz, 4 H), 7.19 (s, 2 H). − MS (CI with H_2O); *m/z* (%): 504 (26) [M^+ + 2], 503 (100) [M^+ + 1], 502 (79) [M^+], 396 (57), 251 (37), 223 (14), 129 (16), 83 (16). − $C_{34}H_{38}N_4$ (502.7): calcd. C 81.24, H 7.62, N 11.15; found C 81.23, H 7.69, N 11.04.

1,3-Dihydro-4,5-bis[methyl(phenyl)amino]-1,3-bis(4-methylphenyl)-2H-imidazol-2-one (**4e**): Yield 60% (0.32 g), colorless crystals, m.p. 172°C, further analytical data are in agreement with literature data.[3]

1,3-Dihydro-4,5-bis[methyl(phenyl)amino]-1,3-bis(4-methylphenyl)-2H-imidazole-2-thione (**4f**): Yield 77% (0.42 g), colorless crystals, m.p. 112°C. − ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 2.36 (s, 6 H), 2.81 (s, 6 H), 6.65 (d, ^3J = 12.6 Hz, 4 H), 6.77 (t, ^3J = 11.7 Hz, 2 H), 7.11−7.23 (m, 8 H), 7.31 (d, ^3J = 13.4 Hz, 4 H). − ^{13}C NMR (CD_2Cl_2, 62 MHz): δ = 21.33, 38.24, 113.79, 119.50, 128.51, 128.90, 129.24, 129.87, 133.62, 139.37, 147.45, 163.01. − MS (CI with H_2O); *m/z* (%): 492 (28) [M^+ + 2], 491 (87) [M^+ + 1], 490 (20) [M^+], 163 (18), 142 (100), 127 (41), 95 (67). − $C_{31}H_{30}N_4S$ (490.6): calcd. C 75.88, H 6.16, N 11.41, S 6.54; found C 75.87, H 6.16, N 11.39, S 6.55.

N-{2-[Methyl(4-methylphenyl)amino]-1,2-bis[methyl(phenyl)-amino]ethenyl}-N-(4-methylphenyl)benzamide (**6b**): Yield 59% (0.37 g), yellow crystals, m.p. 162°C. − IR (KBr): $\tilde{\nu}$ = 1632.1 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.01 (s, 2 H), 2.10−2.36 (m, 4 H), 2.93 (s, 4 H), 3.09 (s, 5 H), 6.57−6.79 (m, 8 H), 6.97−6.99 (m, 8 H), 7.10−7.24 (m, 7 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.41, 20.50, 20.75, 21.16, 29.40, 29.43, 30.28, 34.19, 39.72, 114.90, 115.84, 117.28, 118.04, 118.80, 119.71, 125.26, 125.49, 126.56, 127.40, 128.19, 128.35, 128.52, 129.00, 129.05, 129.48, 129.74, 130.13, 135.19, 135.72, 136.50, 137.82, 139.30, 140.16, 143.20, 144.41, 145.84, 146.71, 170.02. − MS (CI with H_2O); *m/z* (%): 568 (29) [M^+ + 2], 567 (77) [M^+ + 1], 566 (21) [M^+], 461 (31), 460 (11), 253 (65), 237 (17), 221 (67), 205 (45), 165 (100), 125 (11), 105 (21), 93 (57). − $C_{38}H_{38}N_4O$ (566.7): calcd. C 80.53, H 6.76, N 9.89; found C 80.61, H 6.58, N 9.69.

N-{2-[Benzyl(4-methylphenyl)amino]-1,2-bis[methyl(phenyl)-amino]ethenyl}-N-(4-methylphenyl)benzamide (**6c**): Yield 61% (0.43 g), yellow crystals, m.p. 192°C. − IR (KBr): $\tilde{\nu}$ = 1636.5 cm^{-1} (C=O). − ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 2.09 (s, 3 H), 2.24 (s, 3 H), 2.81 (s, 3 H), 3.12 (s, 3 H), 4.68 (s, 1 H), 5.18 (m, 1 H), 6.45 (s, 2 H), 6.67−6.77 (m, 8 H), 7.00−7.21 (m, 18 H). − ^{13}C NMR (CD_2Cl_2, 62 MHz): δ = 20.64, 20.84, 114.96, 117.11, 118.32,

119.41, 120.12, 120.65, 126.47, 127.33, 127.75, 128.00, 128.19, 128.36, 128.67, 128.91, 129.64, 129.75, 130.06, 130.36, 135.99, 136.97, 138.88, 139.59, 143.25, 170.74. − MS (CI with H_2O): *m/z* (%) = 644 (12) [M^+ + 2], 643 (37) [M^+ + 1], 642 (7) [M^+], 270 (16), 269 (100), 223 (11), 194 (11), 137 (29), 105 (14). $C_{44}H_{42}N_4O$ (642.8) calcd. C 82.21, H 6.59, N 8.72; found C 81.56, H 6.88, N 8.62.

☆ Dedicated to Professor *Waldemar Adam*, Würzburg, on the occasion of his 60th birthday.

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[15] Further details of the crystal structure investigations are available on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., on quoting the depository numbers CCDC-407601 (**3e**) and -407600 (**4c**), the names of the authors, and the journal citation.

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